1 604 473

PATENT SPECIFICATION

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(72) Inventors GUY VANLERBERGHE
HENRI SEBAG
JEAN-FRANCOIS GROLLIER and
ALEXANDRE ZYSMAN

(54) PROCESS FOR CONDITIONING THE HEAD OF HAIR

(71) We, L'OREAL, a French body Corporate, of 14 Rue Royale, Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In Specification No. 1,494,915 we have described and claimed a method of conditioning human hair which comprises applying thereto a composition comprising a compatible aqueous or aqueous alcoholic medium and at least one water-soluble crosslinked polymer which is ether (I) a polymer produced by crosslinking a polyamino-polyamide prepared by polycondensation of an acid compound which is either: (i) an organic dicarboxylic acid, (ii) an ethylenically unsaturated aliphatic mono- or dicarboxylic acid, (iii) an ester of an acid as defined under (i) or (ii), (iv) a mixture of two or more compounds as defined under (i), (ii) and (iii), or (v) the product of reaction of a bis-primary amine or a bis-secondary amine with (i), (ii), (iii), or (iv), with a polyamine which is a bis-primary, mono- or di-secondary polyalkylene-polyamine, up to 50 mol % of this polyamine optionally being replaced by a bis-primary amine or a bis-secondary amine, with the proviso that the maximum percentage is 20 mol % when the amine is hexamethylene diamine, the polymer being crosslinked by an epihalohydrin, diepoxide, dianhydride or bis-unsaturated compound, the crosslinking agent being used in an amount from 0.025 to 0.35 mol per amine group of the polyamino-polyamide, or (II) a crosslinked polymer as defined under (I) which has been alkylated (as hereinbefore defined) by an epoxide, ethylenically unsaturated compound, chloroacetic acid, propanesultone or butane sultone, the cross-linked polymer in the composition possessing the following characteristics:

(i) it does not possess any alkylating groups and is chemically stable,
(ii) it is completely soluble in water at a concentration of 10% by weight, without gel formation, and
(iii) the apparent viscosity at a shear rate of 26.3 $secs^{-1}$ of a 10% by weight solution of it in water at 25°C is at least 3 centipoises.

The viscosity of a 10% strength solution in water at 25°C is at least 3 cP and usually 3 to 200 cP.

The compositions for the hair constitute "hair conditioners", which are compatible with anionic shampoos whilst ensuring that wet hair can be combed out satisfactorily and that dry hair possesses good elasticity in order to ensure that the hairstyle holds well.

We have now discovered further cross-linking agents which make it possible to prepare further crosslinked polymers from the polyaminopolyamide (A).

Relative to the polymers and the compositions for the hair which are described in Specification No. 1,494,915, the new polymers and the new compositions in which these polymers are present have the advantage of ensuring that the hair is

generally in a better cosmetic condition and, in particular, of imparting more body and elasticity to dry hair and of improving the hold of the hairstyle.

This advantage is more important in the case of damaged hair which has been subjected to repeated bleaching and/or permanent waving treatments.

The new crosslinking agents can be classed in the following three groups:

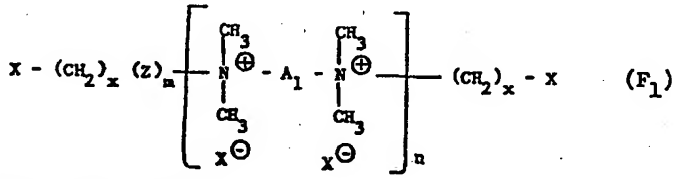
I Simple bifunctional compounds chosen from the group comprising bis-halogenohydrins, bis-azetidinium compounds, bis-halogenoacyldiamines and "bis-(alkyl halides)";

II oligomers obtained by reacting a compound (a), chosen from the groups comprising the bifunctional compounds described in group I above and the bifunctional crosslinking agents described in Specification No 1,494,915, namely epihalogenohydrins, bis-epoxides and bis-unsaturated derivatives, especially epichlorohydrin, N,N'-bis-epoxypropylpiperazine, diglycidyl ether, divinyl sulphone and methylene-bis-acrylamide, with a compound (b) which is a bifunctional compound and reactive towards the compounds (a); and

III the product resulting from the quaternisation of a compound which is chosen from the group comprising the compounds (a) (described in the preceding paragraph) and the oligomers described under (II), and which contains one or more tertiary amine groups which can be totally or partially alkylated, with a known alkylating agent and, in particular, with an alkylating agent chosen from the group comprising methyl or ethyl chlorides, bromides, iodides, sulphates, mesylates and tosylates, benzyl chloride or bromide, ethylene oxide, propylene oxide and glycidol.

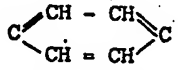
The present invention accordingly provides a process for conditioning human hair which comprises applying thereto a composition comprising a polyamino-polyamide polymer prepared by crosslinking a polyamino-polyamide obtained by the polycondensation of one or more acid compounds, selected from: (i) an organic dicarboxylic acid, (ii) an ethylenically unsaturated aliphatic mono- or di-carboxylic acid, (iii) an ester of an acid as defined under (i) or (ii), (iv), a mixture of two or more compounds defined under (i), (ii) or (iii) or (v) the product of reaction of a bis-primary amine of a bis-secondary diamine with (i), (ii), (iii) or (iv), with one or more polyamines selected from a bis-primary, mono- or di-secondary polyalkylene-polyamine up to 50 mol % of this polyamine optionally being replaced by a bis-primary amine of bis-secondary diamine with the proviso that the maximum percentage is 20 mol % when the amine is hexamethylene diamine, the crosslinking agent being:

(I) Simple bifunctional compounds chosen from the group comprising (1) bis-halogenohydrins resulting from the reaction of an epihalogenohydrin with a primary amine, a bis-secondary diamine, a bis-phenol or a bis-mercaptan, (2) bis-azetidinium compounds, (3) bis-halogenoacyldiamines and (4) compounds represented by the general formula:



(F_1)

in which X=Cl or Br, Z denotes



x=1 to 3, m=0 or 1, and n=0 or 1, it not being possible for m and n to simulaneously denote 1; furthermore, when m=1, x=1; A_1 denotes either a divalent saturated C_2, C_3, C_4 or C_6 hydrocarbon radical or the 2-hydroxypropylene radical;

(II) the oligomers obtained by reacting a compound (a), chosen from the group comprising the compounds (1), (2), (3) and (4) above, (5) epihalogenohydrins, (6) bisepoxides and (7) bis-unsaturated derivatives, with a compound (b) which is a bifunctional compound, reactive towards the compound (a) and chosen from the group comprising primary amines, bis-secondary diamines, bis-mercaptans and bis-phenols, the molar ratio of (b):(a) being from 0.1:1 to 0.9:1;

(II bis) the oligomers obtained by reacting a compound (a_1'), chosen from the group comprising the compounds (1), (3), (4) and (6) above, with a bis-tertiary diamine (b_1) which is a bifunctional compound and reactive towards the compound (a_1), the molar ratio of (b_1):(a_1) being from 0.1:1 to 0.9:1; and

(III) the product resulting from the quaternisation of a compound (a_2), chosen from the group comprising (1) bis-halogenohydrins resulting from the reaction of an epihalogenohydrin with piperazine, a bisphenol of a bis-mercaptan, (2) bis-azetidinium compounds, (3) bis-halogenoacyldiamines, (4) compounds of the formula F_1, (6) bis-epoxides, (7) bis-unsaturated derivatives, (8) the oligomers II obtained by reacting a compound (a_3), chosen from the group comprising the compounds (1), (2), (3), (4), (6) and (7) above, with a compound (b_3) which is a bifunctional compound, reactive towards the compound (a_3) and chosen from the group comprising primary amines, bis, secondary diamines, bis-mercaptans and bis-phenols, the molar ratio of (b_3):(a_3) being from 0.1:L1 to 0.9:1, (9) the oligomers obtained by reacting an epihalogenohydrin (compound a_4) with a bifunctional compound (b_4), chosen from amongst piperazine, bis-mercaptans, bis-phenols and piperazine bis-epoxides, the molar ratio of compound (b_4):epihalogenohydrin being from 0.1:1 to 0.9:1 and (10) the oligomers obtained by reacting a compound (a_5), chosen from the group comprising (1') bis-halogenohydrins resulting from the reaction of an epihalogenohydrin with piperazine, a bis-phenol or a bis-mercaptan, (2) bis-halogenoacyldiamines, (3) compounds of the formula F_1, and (4) bis-epoxides, with a compound (b_5), chosen from the group of the bis-tertiary diamines, the molar ratio of (b_5):(a_5) being from 0.1:1 to 0.9:1, said compound (a_2), containing tertiary amine groups which can be alkylated, with an alkylating agent (c) chosen from the group comprising methyl or ethyl chlorides, bromides, iodides, sulphates, mesylates and tosylates, benzyl chloride or bromide, ethylene oxide, propylene oxide and glycidol.

The simple bifunctional compounds of group I are described in greater detail below.

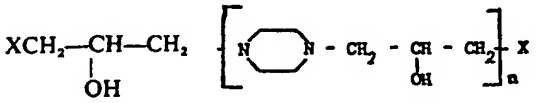
(1) The bis-halogenohydrins obtained by reacting an epihalogenohydrin, such as epichlorohydrin or epibromohydrin, with bifunctional compounds, such as bis-secondary diamines, primary amines, diols, bis-phenols or bis-mercaptans, constitute very valuable crosslinking agents.

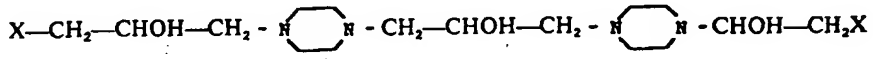
The bis-halogenohydrins resulting from the reaction of epichlorohydrin with piperazine are particularly valuable.

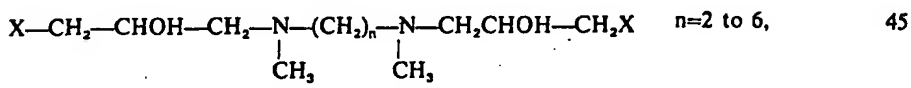
The bis-halogenohydrins can be direct intermediates in the preparation of bis-epoxides but, conversely, they can be derived from the latter by opening the oxirane ring with a hydroacid such as hydrochloric acid of hydrobromic acid.

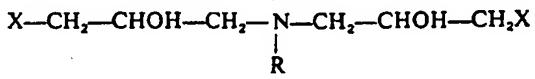
In both cases, the halogen atom can be bonded to the last or penultimate carbon atom without its position being detrimental to the reactivity of the crosslinking agent or to the properties of the final product.

The following bis-halogenohydrins may be mentioned by way of examples:


n=1 to 4,

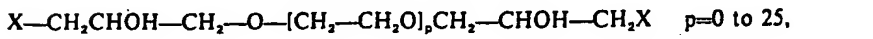


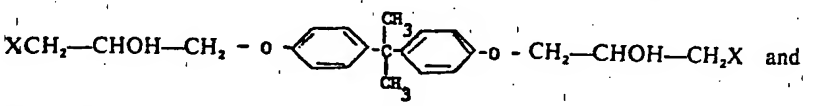

n=2 to 6,



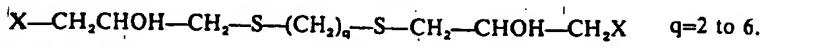
R=C_nH_{2n+1} or also —(CH_2—CH_2—O)$_m$H,

N=1 to 18, and M=1 or 2,


p=0 to 25.



and

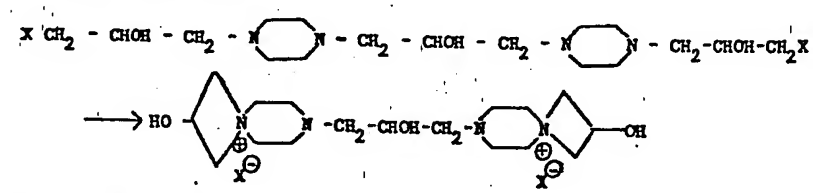


q=2 to 6.

X denotes Cl or Br in the above formulae.

Bis-azetidinium compounds are derived from N,N-dialkylhalogenohydroxypropylamines by cyclisation.

Thus, for example:

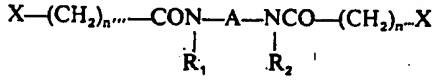


X^- denotes Cl^- or Br^-.

However, the cyclisation can be difficult to carry out for certain sterically-hindered amines.

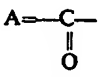
As the reactivity of azetidinium groups is not very different from that of epihalogenohydrin groups, it will be possible, for the purposes of the invention, to use those compounds which are derived from bis-halogenohydrins in which the halogenohydrin units are bonded to the remainder of the molecule by tertiary nitrogen groups, and which contain two azetidinium groups or one azetidinium group and one halogenohydrin group.

The bis-halogenoacyldiamines which can be used as crosslinking agents can be represented by the following formula:

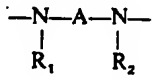


X=Cl or Br, A=$-CH_2CH_2-$, $-CH_2-CH_2-CH_2-$ or

n''' denotes a number from 1 to 10, and $R_1=R_2=H$, or R_1 and R_2 can be bonded to one another and together denote the ethylene radical; when



or $-CH_2-CH_2-CH_2$, $R_1=R_2=H$, the group



denoting the radical

derived from piperazine.

Bis-chloroacetyl-ethylenediamine or -piperazine or bis-bromoundecanoyl-ethylenediamine or -piperazine are particularly valuable for the purposes of the invention.

Piperazine bis-epoxides may be mentioned amongst the particularly valuable bis-epoxides.

Oligomers which can be used include statistical mixtures of compounds obtained by reacting a compound (a), described in groups I and II, or a compound (a_1), described in group II bis, or a compound (a_3) (a_4) or (a_5), described in group III, with a bifunctional compound (b), (b_1), (b_3), (b_4) or (b_5) respectively, which is reactive towards the compounds (a), (a_1), (a_3), (a_4) or (a_5), that is to say, in general terms, primary amines, bis-secondary diamines such as piperazine, bis-tertiary diamines such as N,N,N',N'-tetramethyl-ethylene-, -propylene-, -butylene- or -hexamethylene-diamine, bis-mercaptans such as ethane-1,2-dithiol, or bis-phenols such as "Bis-phenol A" or 2,2'-(4,4'-dihydroxydiphenyl)-propane.

The molar ratios of (b), (b_1), (b_3), (b_4) and (b_5), relative to (a), (a_1), (a_3), (a_4) and (a_5) respectively, are from 0.1:1 to 0.9:1.

The oligomerisation reactions are generally carried out at temperatures of 0 to 95°C, and preferably from 0° to 50°C, in water or in a solvent such as isopropanol, t-butanol, acetone, benzene, toluene, dimethylformamide or chloroform.

The quaternisation reactions, which lead to a quaternisation product as described above under III, are generally carried out at 0 to 90°C in water or in a solvent such as methanol, ethanol, isopropanol, t-butanol, alkoxyethanols, acetone, benzene, toluene, dimethylformamide or chloroform.

Certain of the crosslinked polyamino-polyamide polymers are novel and from the subject of our Application No. 80.24085 (Serial No. 1,604,475). Essentially these polymers are ones in which the crosslinking agent contains one or more piperazino units.

The acids which can be used in the preparation of the polyamino-polyamides (A) are chosen from amongst saturated organic dicarboxylic acids having from 6 to 10 carbon atoms, for example adipic, 2,2,4-trimethyl- and 2,4,4-trimethyl-adipic and terephthalic acids, and aliphatic mono- and di-carboxylic acids containing an ethylenic double bond, for example acrylic, methacrylic and itaconic acids.

The preferred acids include adipic acid and the compounds resulting from the addition of an alkylenediamine to unsaturated acids such as acrylic, methacrylic and itaconic acids.

Adipic acid is particularly preferred.

Esters of the abovementioned acids can also be used. It is also possible to use mixtures of two or more carboxylic acids and of their esters.

Polyamines which can be used in the preparation of the polyamino-polyamides (A) are chosen from amongst bis-primary, mono- or di-secondary polyalkylene-polyamines, for example diethylenetriamine, dipropylenetriamine and triethylenetetramine and their mixtures.

Polycondensation is carried out by known processes, by mixing the reactants and then heating them at, say, 80° to 250°C, and preferably 100 to 180°C, for 1 to 8 hours depending on the reactants used. After heating under total reflux for ½ hour to 1 hour, the water or the alcohol formed during the polycondensation is removed, first at ordinary pressure and then under reduced pressure.

The reactions take place under a stream of nitrogen in order to avoid excessive colorations and to facilitate the removal of the volatile substances.

When carrying out the reaction, the amount of dicarboxylic acid and amines used is preferably such that they are in equimolar proportions.

According to a preferred method of preparation, the polycondensation of the polyalkylene-polyamine, which is preferably chosen from amongst diethylenetriamine, triethylenetetramine, dipropylenetriamine and their mixtures, is carried out either (i) with a dicarboxylic acid, preferably adipic acid or its dimethyl ester, or (ii) with the intermediate product resulting from the addition of one molecule of ethylenediamine to two molecules of the methyl ester of an ethylenically unsaturated acid, such as methyl acrylate, methacrylate or itaconate.

The reactions involving the addition of ethylenediamine to unsaturated esters are suitably carried out by mixing the reactants at 5° to 80°C, and the polycondensation reactions are carried out by heating under reflux for 30 to 60 minutes, followed by removal of methyl alcohol at 120—150°C or of water at 140—175°C, first at ordinary pressure and then under a partial vacuum of 15 mm of mercury.

The polyamino-polyamides (A) thus obtained have a viscosity, as a 10% strength solution in water and at 25°C, of less than 3 centipoises.

The structure of the preferred polyamino-polyamides (A) can be represented by the general formula (I)

$$—[—OC—R—CO—Z—]— \qquad (I)$$

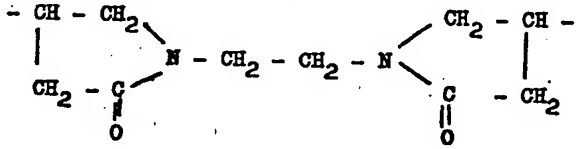
in which R represents a divalent radical which is derived from the acid used or from the product resulting from the addition of the acid to the bis-primary or bis-secondary amine.

Amongst the preferred meanings of R, the following may be mentioned:

$$-(CH_2)_4-,$$

$$-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-,$$

$$-CH(CH_3)-CH_2-NH-CH_2-CH_2-NH-CH_2-CH(CH_3)- \text{ and}$$



These radicals are derived respectively from terephthalic acid, from adipic acid and from the product resulting from the addition of ethylenediamine to acrylic, methacrylic and itaconic acids or their esters.

Z represents:

1) in proportions of 60 to 100 mol %, the radical

$$-NH-[(CH_2)_x-NH-]_n \qquad (II)$$

in which x=2 and n=2 or 3, or x=3 and n=2, this radical being derived from diethylenetriamine, triethylenetetramine or dipropylenetriamine;

2) in proportions of 0 to 40 mol %, the above radical (II), in which x=2 and n=1, and which is derived from ethylenediamine, or the radical

derived fron piperazine; and

3) in proportions of 0 to 20 mol %, the radical $-NH-(CH_2)_6-NH-$, derived from hexamethylenediamine.

The polyamino-polyamides thus obtained are then crosslinked by adding a crosslinking agent chosen from amongst those described above.

The crosslinking reactions are generally carried out at 20°C to 90°C, starting from 20 to 30% strength aqueous solutions of polyaminopolyamide, to which the crosslinking agent is added in very small portions until a large increase in the viscosity is obtained, but without however reaching the stage of a gel which would no longer dissolve in water. The concentration is then rapidly adjusted to 10% by adding water, and the reaction mixture is cooled if necessary.

According to a preferred characteristic of the invention, from 0.025 to 0.35 mol of crosslinking agent per amine group of the polyamino-polyamide is employed for crosslinking the polyamino-polyamide polymers. A valuable category of these crosslinked polymers is obtained by using from 0.025 to about 0.2 mol of crosslinking agent per amine group of the polyamino-polyamide. A further advantageous category of crosslinked polymers is obtained by using from 0.025 to about 0.1 mol of crosslinking agents per amine group of the polyamino-polyamide.

The proportions of crosslinking agent to be used, which vary depending on the nature of the polyaminopolyamide and of the crosslinking agent, can be determined easily by adding the desired crosslinking agent to an aqueous solution of the polyamino-polyamide until the viscosity of a 10% strength solution, at 25°C, is between 3 centipoises and the gel state, whilst retaining perfect solubility in water.

In fact the crosslinked polymer possesses all the following characteristics:

(I) it is perfectly soluble in water to a concentration of 10% without gel formation;

(2) the viscosity of a 10% strength solution of the polymer in water at 25°C is at least 3 centipoises; and
(3) it does not possess any reactive group and, in particular, it does not have any alkylating property and is chemically stable.

The crosslinked polymers used according to the present invention can be stored satisfactorily and are compatible with anionic surface-active agents, whilst ensuring that wet hair can be combed out easily. This compatibility with an anionic surface-active agents can be further improved by alkylating the secondary amine groups of the crosslinked polyamino-polyamides. Alkylation increases the solubility in water of the crosslinked polyamino-amides, in the presence of anionic surface-active agents.

The following can be used as the alkylating agent:
1) an epoxide, for example glycidol, ethylene oxide or propylene oxide;
2) a compound containing an ethylenic double bond, for example acrylamide or acrylic acid;
3) chloroacetic acid; or
4) an alkane sultone, for example propane sultone or butane sultone.

The alkylation of the crosslinked polyamino-amides is suitably carried out in aqueous solution, at a concentration of 10 to 30% and at a temperature of between 10 and 95°C.

The crosslinked polymers used according to the invention can be used in various cosmetic compositions for the hair, for the treatment of normal hair and more particularly of sensitised hair. They can also be used at concentrations of 0.1 to 5%, preferably from 0.2 to 2.5% and advantageously from 0.3 to 1.3%, in cosmetic compositions for the hair and more particularly in shampoo compositions such as an anionic, cationic, non-ionic, amphoteric or zwitterionic shampoo, colouring shampoo compositions, dyeing compositions, styling, gel compositions, styling lotion compositions, "brushing" lotion compositions, wavesetting lotion compositions, rinsed lotion (rinse) compositions and non-rinsed reinforcing wave-setting lotion compositions, in restructuring compositions and in more specific cosmetic compositions such as anti-dandruff, anti-seborrhoea and permanent waving compositions.

Certain cosmetic composition for the hair used in the process of the present invention are novel and these form the subject of our Application No. 80.24084 (Serial No. 1,604,474). These compositions comprise, in aqueous, alcoholic or aqueous alcoholic medium, a crosslinked polyamino-polyamide as defined for the process of this invention, said composition comprising at least one cosmetic adjuvant which is one or more electrolytes, foam stabilisers, hair strengthening agents, perfumes, colorants, preservatives, sequestering agents, thickeners, emulsifiers, anionic, cationic, amphoteric, zwitterionic of non-ionic surface-active agents, synergistic agents, softening agents or cosmetic resins.

The cosmetic compositions for the hair used in the present invention generally have a pH of 2 to 11 and preferably 3 to 8.

Those cosmetic compositions for the hair which are to be applied to sensitised hair, advantageously contain an electrolyte. The presence of the electrolyte in the composition reduces or eliminates the tendency of sensitised hair to retain the polymers for a long time. Water-soluble alkali metal or alkaline earth metal salts of inorganic or organic acids, preferably the chlorides and acetates of sodium, potassium, ammonium and calcium, are used as electrolytes. The amount of electrolyte is not critical. It is preferably from 0.01 to 5%, and advantageously from 0.4 to 3%, of the total weight of the composition. The ratio of electrolyte:polymer is suitably 0:1 to 1.5:1.

The cosmetic compositions for the hair can be coloured and generally contain from 0.001 to 0.5% of colorants, relative to the total weight of the composition. In addition, they usually contain a perfume in a proportion of 0.1 to 0.5% of the total weight of the composition.

In the compositions, the crosslinked polyamino-amides are usually present at the rate of 0.1 to 5%, and preferably 0.1 to 3%, by weight, relative to the total weight of the composition.

The compositions for the hair can be in the form of, for example, aqueous or aqueous-alcoholic solutions (the alcohol being a lower alkanol such as ethanol or isopropanol), or in the form of creams, gels, dispersions of emulsions.

In addition to the crosslinked polyamino-polyamides, the cosmetic compositions generally comprise various adjuvants which are usually employed in cosmetic compositions for the hair. The adjuvants which are generally present in

these cosmetic compositions are, for example, perfumes, colorants, preservatives, sequestering agents, thickeners, emulsifiers, anionic, cationic, amphoteric, zwitterionic or non-ionic surface-active agents, synergistic agents, softening agents and cosmetic polymers or resins, in particular non-ionic or cationic polymers or resins.

The cosmetic compositions for the hair constitute, in particular, treatment creams to be applied before or after colouring or bleaching, before or after shampooing, or before or after permanent waving, colouring products shampoos, rinsed lotions to be applied before or after shampooing, wavesetting lotions, brushing lotions and structuring lotions.

When the compositions constitute treatment creams to be applied before or after colouring or bleaching, before or after shampooing, or before or after permanent waving, the formulation of these carriers is based on soaps or fatty alcohols, in the presence of emulsifiers. They can additionally contain fatty amides, glycerol, polymers, perfumes and colorants.

The pH of these creams is generally 3 to 9, and preferably 5 to 9.

The soaps can be formed from natural or synthetic C_{12}—C_{18} fatty acids (such as lauric acid, myristic acid, palmitic acid, oleic acid, ricinoleic acid, stearic acid and isostearic acid), at concentrations of, say, 10 to 30%, and from alkalising agents (such as sodium hydroxide, potassium hydroxide,ammonia, monoethanolamine, diethanolamine and triethanolamine).

The fatty amides which can be used include the following compounds in particular: the mono- or di-ethanolamides of acids derived from copra, of lauric acid or of oleic acid, at concentrations of up to, say, 10%.

Fatty alcohols which can be used include, in particular, oleyl, tetradecyl, cetyl, stearyl and isostearyl alcohols, at concentrations of up to, say, 10%.

The creams can also be formulated from natural or synthetic C_{12}—C_{18} alcohols mixed with emulsifiers. Amongst the fatty alcohols, there may be mentioned in particular: the alcohol derived from copra fatty acids, tetradecyl alcohol, cetyl alcohol, stearyl alcohol and hydroxystearyl alcohol, at concentrations of between 5 and 25%.

The emulsifiers can belong to the following classes:

Non-ionic surface-active agents such as oxyethyleneated or polyglycerolated fatty alcohols, such as, for example, polyoxyethyleneated oleyl alcohol containing 10 mols of ethylene oxide, oxyethyleneated cetyl alcohol containing 6 to 10 mols of ethylene oxide, oxyethyleneated cetyl/stearyl alcohol containing 10 mols of ethylene oxide, stearyl alcohol containing 10—15 or 20 mols of ethylene oxide, polyglycerolated oleyl alcohol containing 4 mols of glycerol, and polyoxyethyleneated synthetic C_9—C_{15} fatty alcohols containing 5 or 10 mols of ethylene oxide. These "non-ionics" are suitably present at the rate of 5 to 25% by weight.

Anionic surface-active agents such as alkyl-sulphates which may or may not br oxyethyleneated, such as sodium lauryl-sulphate, ammonium lauryl-sulphate, sodium cetyl-/stearyl-sulphate, triethanolamine cetyl-/stearyl-sulphate, monoethanolamine laurylsulphate, oxyethyleneated sodium lauryl-ether-sulphate (containing, for example, 2.2 mols of ethylene oxide) and oxyethylenated monoethanolamine laurylether-sulphate (containing, for example, 2.2 mols of ethylene oxide). These constituents are generally present at concentrations of 3 to 15% by weight.

Oleyl diethanolamide, copra mono- or di-ethanolamide and stearyl monoethanolamide may be mentioned as examples of fatty amides. These amides are used at concentrations of up to, say, 10%.

When the compositions constitute colouring creams, they comprise, in addition to the crosslinked polyamino-amide, various ingredients which make it possible to form creams as defined above, to which an alkalising agent and colorants are added.

The pH of these compositions is generally from 9 to 11 and it can be adjusted by adding a suitable alkalising agent to the dyeing carrier, for example by adding ammonia, mono-ethanolamine, diethanolamine or triethanolamine.

The colorants are typically oxidation dyestuffs, to which direct dyestuffs, such as azo dyestuffs, anthraquinone dyestuffs, nitro-derivatives of the benzene series, indamines, indoanilines, indophenols, or other oxidation dyestuffs such as the leuco-derivatives of these compounds, can be added.

When the compositions constitute shampoos, they comprise, in addition to

the crosslinked polyamino-amide polymer, at least one anionic, cationic, non-ionic or amphoteric detergent.

Amongst the anionic surface-active agents, the following compounds, as well as their mixtures, may be mentioned in particular:

the alkali metal salts, magnesium salts, ammonium salts, amine salts or aminoalcohol salts of the following compounds:

alkyl-sulphates, alkyl-ether-sulphates, of which the alkyl has a linear C_{12} to C_{18} chain, oxyethyleneated alkylamide-sulphates and ether-sulphates having linear C_{12} to C_{18} chains, alkylaryl-polyether-sulphates and monoglyceride-sulphates,

alkylsulphonates, of which the alkyl has a linear C_{12} to C_{18} chain, alkylamide-sulphonates, alkylarylsulphonates, and alpha-olefin-sulphonates having linear C_{12} to C_{16} chains,

alkylsulphosuccinates, alkyl-ether-sulphosuccinates, and alkyl-amide-sulphosuccinates, of which the alkyl has a linear C_{12}—C_{18} chain,

alkylsulphosuccinamates, of which the alkyl has a linear C_{12} to C_{18} chain,

alkylsulphoacetates, of which the alkyl has a C_{12} to C_{18} chain,

alkyl-phosphates, and alkyl-ether-phosphates, of which the alkyl has a C_{12} to C_{18} chain,

alkylsarcosinates, alkylpolypeptidates, alkylamidopolypeptidates, alkylisethionates, and alkyl-taurates, of which the alkyl has a C_{12} to C_{18} chain, and

fatty acids such as oleic acid, ricinoleic acid, palmitic acid, stearic acid, acids of copra oil or of hydrogenated copra oil, carboxylic acids, and carboxylic acids of polyglycol ethers of the formula $Alk—(OCH_2—CH_2)_n—OCH_2—CO_2H$, in which Alk is a C_{12} to C_{18} linear chain and n is an integer from 5 to 15.

Amongst the cationic surface-active agents which can be used by themselves or in mixtures, there may be mentioned in particular: fatty amine salts such as alkylamine acetates, quaternary ammonium salts such as the chlorides and bromides of alkyldimethylbenzylammonium, alkyltrimethylammonium, alkylmethylhydroxyethylammonium and dimethyldistearylammonium, and alkylamidoethyltrimethylammonium methosulphates, alkylpyridinium salts and imidazoline derivatives.

Amine oxides having a cationic character, such as alkyldimethylamine oxide or alkylaminoethyldimethylamine oxide, may also be mentioned.

Amongst the non-ionic surface-active agents which can optionally be used in mixtures with the abovementioned anionic surface-active agents, there may be mentioned: products resulting from the condensation of a monoalcohol, an α-diol, an alkylphenol or an amide with glycidol, for example compounds of the formula $R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$, in which R denotes an aliphatic, cycloaliphatic or arylaliphatic radical having from 7 to 21 carbon atoms, and their mixtures, it being possible for the aliphatic chains to contain ether, thioether and hydroxymethylene groups, and in which $1 \leqslant n \leqslant 10$, and compounds of the formula $RO[C_2H_3O(CH_2OH)]_nH$, in which R denotes an alkyl, alkenyl or alkylaryl radical having from 8 to 22 carbon atoms and n denotes a number between 1 and 10, polyoxyethyleneated or polyglycerolated alcohols, alkylphenols or fatty acids having a linear C_8 to C_{18} fatty chain and most frequently containing from 2 to 15 mols of ethylene oxide, for example polyoxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide, ethylene oxide/propylene oxide copolymers, condensates of ethylene oxide and of propylene oxide with fatty alcohols, polyoxyethyleneated fatty amides, polyoxyethyleneated fatty amines, ethanolamides, glycol fatty acid esters, sorbitol fatty acid esters and sucrose fatty acid esters.

Amongst the amphoteric surface-active agents which can be used, there may be mentioned in particular: alkylamino-mono- and -di-propionates, betaines such as N-alkylbetaines, N-alkylsulphobetaines and N-alkylamidobetaines, and cycloimidinium compounds (alkylimidazolines).

All these detergents, as well as numerous other detergents which can be used in the shampoos are well known and are described in the literature.

The compositions in the form of shampoos can also contain various adjuvants such as, for example, perfumes, colorants, preservatives, thickeners, foam stabilisers, softening agents and cosmetic resins.

Amongst the foam stabilisers, there may be mentioned fatty amides and, in particular, copra mono- or di-ethanolamides and lauryl mono- or di-ethanolamides.

In these shampoos, the concentration of detergent is generally from 3 to 50%, and preferably from 3 to 20%, by weight, relative to the total weight of the composition, and the pH is generally from 3 to 9.

When the compositions constitute lotions, they can be hair-styling lotions, shaping lotions (called "brushing lotions"), non-rinsed reinforcing wavesetting lotions or rinsed lotions (called "rinses"), for example.

The term shaping lotion or "brushing lotion" is to be understood as meaning a lotion which is applied after the shampoo and which assists the shaping of the head of hair, this shaping process being carried out on wet hair, using a brush, at the same time as the hair is dried using a hand-held drier.

The term non-rinsed reinforcing wavesetting lotion is to be understood as meaning a lotion which is applied after shampooing and before wavesetting; this lotion, which is not removed by rinsing, facilitates the subsequent wavesetting process and lengthens the time for which the hair holds its set.

These lotions comprise, in aqueous, alcoholic or aqueous-alcoholic solution, at least one crosslinked polyaminoamide as defined above. They can additionally contain: film-forming polymers such as polyvinylpyrrolidone, polyvinylpyrrolidone/vinyl acetate copolymers, and copolymers resulting from the copolymerisation of vinyl acetate with a vinyl alkyl ether.

Amongst the preferred resins, there may be mentioned polyvinylpyrrolidone having a molecular weight of 10,000 to 70,000, polyvinylpyrrolidone (PVP)/vinyl acetate (VA) copolymers having a molecular weight of 30,000 to 200,000, the ratio of PVP:VA being between 30:70 and 70:30, and methyl methacrylate (15—25%)/stearyl methacrylate (18—28%)/dimethylaminoethyl methacrylate (52—62%) terpolymers which may or may not be quaternised by methyl sulphate,

quaternary polyvinylpyrrolidone copolymers such as, for example, the polymer having a molecular weight of the order of 1,000,000 and sold under the trademark "Gafquat 755" by GAF Corporation, and the polymer having a molecular weight of the order of 100,000 and sold under the trademark "Gafquat 734" by GAF Corporation, cationic graft copolymers resulting from the copolymerisation of 3 to 95% by weight of N-vinylpyrrolidone, 3 to 95% by weight of dimethylaminoethyl methacrylate and 2 to 50% by weight of polyethylene glycol, such as those described in French Patent No. 76/15,948, cationic polymers resulting from the condensation of piperazine or of its derivatives (1) with bifunctional compounds such as alkyl or alkylaryl dihalides, bis-epoxides, epihalogenohydrins or bisunsaturated derivatives, (2) with a primary amine, and two hydrogen atoms of which can be substituted and which behaves as a bifunctional compound, or (3) both with an epihalogenohydrin and with a hydroxylated amine such as diglycolamine or 2 - amino - 2 - methylpropane - 1,3 - diol, or with an aminoacid such as glycocoll, and quaternised celluloses such as "JR 400" sold by Messrs. Union Carbide.

In these lotions, the concentration of polymer is generally from 0.1 to 5%, and preferably from 0.1 to 3%, and the pH is generally from 3 to 9.

The term rinsed lotion is to be understood as meaning a lotion which is applied before or after colouring or bleaching, before or after shampooing or between the two stages of shampooing, or before or after permanent waving, in order to obtain a hair conditioning effect, and which is rinsed out after remaining on the hair for a period of time.

These compositions can be aqueous or aqueous-alcoholic solutions which may or may not comprise surface-active agents, or they can be emulsions of gels.

These compositions can be pressurised in the form of an aerosol. Surface-active agents which can be used in the rinsed lotions are principally non-ionic of cationic surface active agents such as those described in the composition of the shampoos, and more particularly: products resulting from the condensation of a monoalcohol, an alpha-diol, an alkylphenol or an amide with glycidol, for example compounds of the formula $R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$, in which R denotes an aliphatic, cycloalkphatic or arylaliphatic radical having from 7 to 21 carbon aroms, and their mixtures, it being possible for the aliphatic chains to contain ether, thioether and hydroxymethylene groups, and in which $1 \leqslant n \leqslant 10$, and compounds of the formula $RO[C_2H_3O(CH_2OH)—]_n—H$, in which R denotes an alkyl, alkenyl or alkylaryl radical having from 8 to 22 carbon atoms and n is between 1 and 10, and polyoxyethyleneated or polyglycerolated alcohols, alkylphenols or fatty acids having a linear C_8 to C_{18} fatty chain and most frequently containing from 2 to 15 mols of ethylene oxide.

The concentration of surface-active agents in the rinsed lotions can generally vary up to 7%.

Anionic or amphoteric surface-active agents can also be added.

When the compositions are in the form of emulsions, they can be non-ionic or

anionic. The non-ionic emulsions comprise a mixture of oils and/or of waxes, fatty alcohols, and polyoxyethyleneated fatty alcohols such as polyoxyethyleneated stearyl or cetyl/stearyl alcohols, for example, containing 10 mols of ethylene oxide. Cationics such as those defined above can be added to these compositions.

The anionic emulsions are formed from soaps. Thus, there may be mentioned the emulsion comprising self-emulsifying glycerol stearate sold under the tradename Imwitor 960 K by Messrs. Dynamit Nobel, and the emulsions comprising a combination of glycerol monostearate with citric acid esters, with fatty alcohols and lipopeptides or with alkali metal stearates, sold respectively under the tradenames Lameform ZEM, PLM and NSM by Messrs. Grunau.

When the compositions are in the form of gels, they contain thickeners which may or may not be in the presence of solvents.

The thickeners can be sodium alginate, gum arabic, cellulose derivatives such as methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose and carboxymethylcellulose, or carboxylic polymers such as the "Carbopols" (Registered Trade Mark). It is also possible to obtain a thickener for the lotions by mixing polyethylene glycols with polyethylene glycol stearates or distearates, or by mixing phosphoric esters with amines.

The concentration of thickener is generally from 0.5 to 30%, and preferably from 0.5 to 15%, by weight.

The pH of the rinsed lotions generally varies from 2 to 9.5.

When the compositions constitute restructuring lotions, they contain products which strengthen the keratin chain of hair.

Methylol-type derivatives, such as those described in French Patents Nos. 1,527,085 and 1,519,979, belong to this class of products.

The present invention is further illustrated by the following Examples. Examples I to X illustrate the preparation of polymers used in the invention.

Prepparation Examples

EXAMPLE A

Polycondensation of adipic acid with diethylenetriamine in equimolar amounts.

The structure of the polymer obtained can be characterised by the following unit:

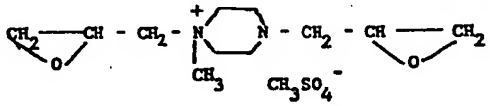
$$-[-OC-(CH_2)_4-CONH-(CH_2-CH_2-NH)_2-]-$$

876 g (6 mols) of adipic acid are added, whilst stirring and in a nitrogen atmosphere, to 619 g (6 mols) of diethylenetriamine, in the course of 15 minutes. The reaction mixture is then heated to 145—150°C, at which temperature condensation of water is observed. Refluxing is maintained for 45 minutes and the water is then removed by distillation at ordinary pressure for 2 hours and then under reduced pressure (15 mm Hg) for 1 hour. The heating temperature gradually increases to 170°C.

The product thus obtained is cast whilst hot. After cooling, it is in the form of a hard and brittle resin. The resin is a transparent yellow-green colour and dissolves completely in water.

EXAMPLE Ia

Preparation of the quaternised crosslinking agent of the formula:



36.4 g (0.289 mol) of dimethyl sulphate are added, in the course of one hour, to 236 g of a chloroform solution containing 57.2 g (0.289 mol) of bis-(epoxypropyl)-piperazine, whilst stirring the reaction medium at 30°C.

The quaternised derivative is then precipitated from its solution with a large excess of ether. After drying, a very viscous oil is collected. Its epoxide content is 5.19 milliequivalents/g.

EXAMPLE Ib

Crosslinking, using the crosslinking agent prepared in Example Ia, of the

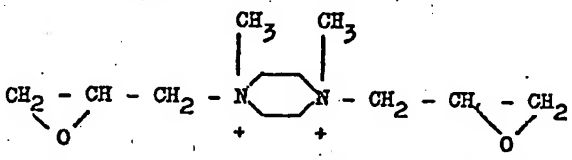
polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

22 g (0.057 mol) of the quaternised crosslinking agent prepared in Example Ia are added, at ambient temperature, to 500 g of an aqueous solution containing 100 g (0.585 equivalent of amine) of the polyamine-amide prepared by condensing adipic acid with diethylene triamine in equimolar amounts, according to Example A, and the temperature of the reaction medium is then brought to 90°C.

After 20 minutes, gelling of the solution is observed. 698 g of water are then added rapidly. A clear yellow-green coloured solution containing 10% of active material is obtained. The viscosity, measured at 25°C and at a rate of shear of 87.93 seconds^{-1}, is 0.68 P.

EXAMPLE IIa

Preparation of the quaternised crosslinking agent of the formula:



70 g (0.555 mol) of dimethyl sulphate are added, in the course of one hour, to 187.3 g of a chloroform solution containing 54.9 g (0.277 mol) of bis-(epoxypropyl)-piperazine, whilst stirring the reaction medium at 30°C.

The medium thickens during the addition and solidifies after several hours at ambient temperature. The paste is dissolved in hot dimethylformamide. When cold, the solution yields white crystals having a melting point of 205°C and an epoxide number of 4.25 milliequivalents/g.

EXAMPLE IIb

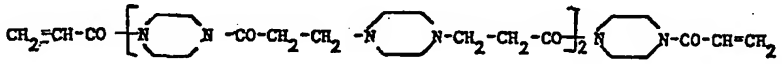
Crosslinking, using the crosslinking agent prepared in Example IIa, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

20 g (0.0425 mol) of the crosslinking agent prepared above are added, at ambient temperature, to 476 g of an aqueous solution containing 95.2 g (0.557 equivalent of amine) of the polyamino-amide prepared according to Example A. The reaction mixture is stirred at 90°C for 1 hour and the concentration of active material in the solution is brought back to 10% by adding 656 g of water.

The solution is a clear yellow-green colour. The viscosity, measured at 25°C and at a rate of shear of 87.93 seconds^{-1}, is 0.27 P.

EXAMPLE IIIa

Preparation of a bis-unsaturated oligomeric crosslinking agent which is obtained from piperazine bis-acrylamide and piperazine in the molar proportions of 3/2 and which has the formula:



223 g of an aqueous solution containing 56.8 g (0.66 mol) of piperazine are added, in the course of one hour and at between 10 and 15°C, to 380 g of an aqueous solution containing 194 g of bis-acrylamide (1 mol). The reaction medium is then left for 24 hours at ambient temperature. The solution becomes turbid and thickens. It is clarified by heating and is then run dropwise into 5 litres of acetone. The crosslinking agent precipitates. After filtration and drying, a white solid is collected, which has a solids content of 80%.

EXAMPLE IIIb

Crosslinking, using the crosslinking agent prepared in Example IIIa, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

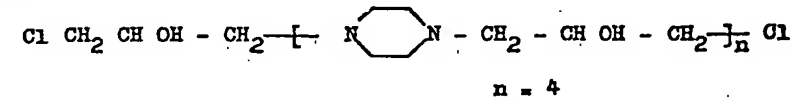
50 g of the crosslinking agent prepared above are added, at ambient temperature, to 370 g of an aqueous solution containing 111 g (0.649 equivalent of

amine) of the polyamino-amide prepared according to Example A, and the temperature of the reaction medium is then brought to 90°C. After 30 minutes, the medium gels. The solids content of the solution is rapidly brought back to 10% by adding 1,050 g of water.

A clear yellow-green solution is obtained, which has a viscosity, measured at 25°C, of 58 centipoises.

EXAMPLE IVa

Bis-halogenohydrin oligomeric crosslinking agent which is prepared from epichlorohydrin and piperazine in the molar proportions of 5/4 and which has the formula:



n = 4

92.5 g (1 mol) of epichlorohydrin are added, in the course of one hour and without exceeding 20°C, to 541 g of an aqueous solution containing 69.4 g (0.806 mol) of piperazine. The reaction medium is stirred for a further one hour at 20°C and 60 g (0.6 mol) of a 40% strength sodium hydroxide solution are then added at the same temperature, in the course of one hour.

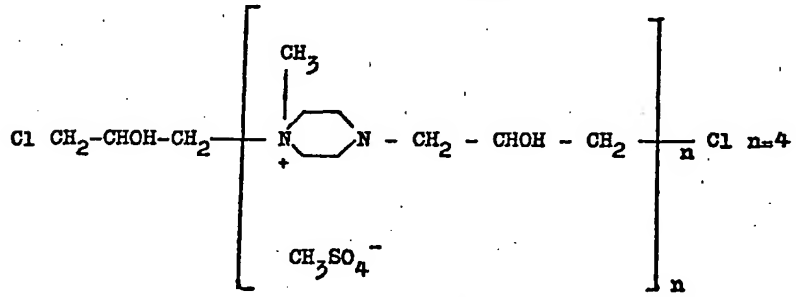
EXAMPLE IVb

Crosslinking, using the crosslinking agent prepared in Example IVa, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

268 g of an aqueous solution contining 54.9 g of the crosslinking agent prepared above are added, at ambient temperature, to 787.5 g of an aqueous solution containing 157.5 g (0.92 milliequivalent of amine) of the polyamino-amide prepared according to Example A. The temperature of the reaction medium is kept at 90°C for 4 hours 50 minutes. Gelling is then observed. By rapidly adding 1,100 cc of water, a clear solution is obtained, which contains 9.85% of active material and has a viscosity, measured at 25°C, of 73 centipoises.

EXAMPLE Va

Preparation of the quaternised crosslinking agent of the formula:



47.4 g (0.376 mol) of dimethyl sulphate are added, in the course of one hour and without exceeding 30°C, to 330 g of an aqueous solution containing 67.7 g (0.752 equivalent of amine) of the crosslinking agent prepared in Example IVa. The reaction medium is stirred for a further 2 hours at this temperature.

EXAMPLE Vb

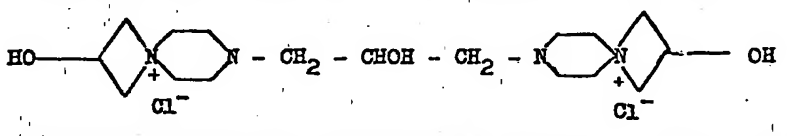
Crosslinking, using a crosslinking agent prepared in Example Va, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

155 g of an aqueous solution containing 47.25 g of the crosslinking agent prepared above are added, at ambient temperature, to 327.7 g of an aqueous solution containing 65.5 g (0.383 equivalent of amine) of the polyamino-amide prepared according to Example A. After heating at 85°C for 4 hours, the reaction medium gels.

By rapidly adding 745 g of water, a clear solution containing 10% of active material is obtained. The viscosity, measured at 25°C and at a rate of shear of 67.18 seconds^{-1}, is 0.47 Poise.

EXAMPLE VIa

Preparation of the bis-azetidinium crosslinking agent of the formula:



43.5 g (0.47 mol) of epichlorohydrin are added, at between 0 and 5°C, to 50 g (0.212 mol) of bis - 1,3 - piperazine propan - 2 - ol, prepared by adding epichlorohydrin to piperazine in accordance with Example 15 of British Specification No. 1,416,454 which are dissolved in 100 g of absolute alcohol. The reaction medium is left for 24 hours at 0°C and the crosslinking agent is then precipitated from its solution with a large excess of ether. A white solid having a softening point of about 120°C is isolated.

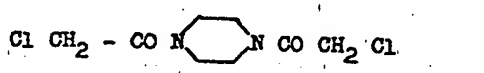
EXAMPLE VIb

Crosslinking, using a crosslinking agent prepared in Example VIa, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

15.4 g (0.036 mol) of the crosslinking agent prepared above are added, at ambient temperature, to 386 g of an aqueous solution containing 77.2 g (0.452 equivalent of amine) of the polyamino-amide of Example A. After heating at 90°C for 2 hours 30 minutes, the medium gels. By rapidly adding 525 g of water, a clear solution containing 10% of active material is obtained. The viscosity, measured at 25°C and at a rate of shear of 67.18 seconds^{-1}, is 0.7 Poise.

EXAMPLE VIIa

Preparation of the bis-(chloroacetyl)-piperazine crosslinking agent of the formula:



This crosslinking agent is prepared by condensing 2 molecules of chloroacetyl chloride with one molecule of piperazine in the presence of sodium hydroxide.

EXAMPLE VIIb

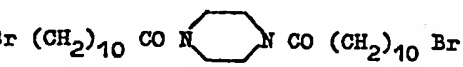
Crosslinking, using the crosslinking agent prepared in Example VIIa, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

24 g (0.1 mol) of bis-(chloroacetyl)-piperazine are added, at ambient temperature, to 1,000 g of an aqueous solution containing 200 g (1.170 equivalents of amine) of the polyamino-amide of Example A, and the temperature of the reaction medium is then brought to 90°C. After heating for 30 minutes, gelling of the medium is observed.

1.216 g of water are added rapidly and the heating is continued at 80°C for one hour. A clear solution is obtained, which contains 10% of active material and has a viscosity, measured at 25°C and at a rate of shear of 88.41 seconds^{-1}, of 0.29 Poise.

EXAMPLE VIIIa

Preparation of the bis-(1,1-bromoundecanoyl)-piperazine crosslinking agent of the formula:



This crosslinking agent is prepared by condensing 2 molecules of bromoundecanoyl bromide with 1 molecule of piperazine in the presence of sodium hydroxide.

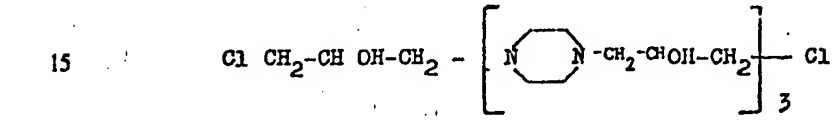
EXAMPLE VIIIb

Crosslinking, using the crosslinking agent prepared in Example VIIIa, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

60 g of an isopropanol solution containing 10 g (0.017 mol) of bis-(1,1 - bromoundecanoyl)-piperazine are added, at ambient temperature, to 113.3 g of an aqueous solution containing 56.7 g (0.33 equivalent of amine) of the polyamino-amide of Example A. the reaction medium is heated at the reflux temperature of the solvent for 2 hours 30 minutes. The isopropanol is then distilled, whilst adding water until a concentration of 10% of active material in the aqueous solution of resin is obtained. The solution is slightly opalescent and its viscosity, measured at 25°C and at a rate of shear of 87.93 seconds^{-1}, is 0.052 Poise.

EXAMPLE IXa

Preparation of an oligomeric crosslinking agent of the formula:



from epichlorohydrin and piperazine in the molar proportions of 4/3.

246.7 g (2.66 mols) of epichlorohydrin are added, in the course of 1 hour, to 1,149 g of an aqueous solution containing 172 g (2 mols) of piperazine, whilst stirring the reaction medium at 20°C.

After stirring for a further one hour at 20°C, 133 g (1.33 mols) of a 40% strength sodium hydroxide solution are added at the same temperature and in the space of one hour. Precipitation is observed during the neutralisation. 638 g of water are added and the mixture is heated for a few minutes at 50°C in order to obtain a clear solution.

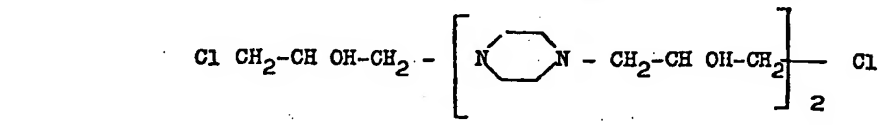
EXAMPLE IXb

Crosslinking, using the crosslinking agent prepared in Example IXa, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

584 g of an aqueous solution containing 99.8 g of the crosslinking agent prepared in Example IXa, are added to 2,000 g of an aqueous solution containing 400 g (2.34 equivalents of amine) of the polyamino-amide prepared according to Example A, and the reaction medium is then stirred at 90°C for 5 hours. 2,414 g of water are then added in order to obtain a clear solution, which contains 10% of active material and has a viscosity, measured at 25°C, of 0.22 Poise.

EXAMPLE Xa

Preparation of an oligomeric crosslinking agent of the formula:



from epichlorohydrin and piperazine in the molar proportions of 3/2.

277.5 g (3 mols) of epichlorohydrin are added, in the course of 1 hour and at 20°C, to 1,221 g of an aqueous solution containing 172 g (2 mols) of piperazine, whilst stirring the reaction medium at 20°C. After stirring for a further one hour, 100 g (1 mol) of a 40% strength solution of sodium hydroxide in water are added at a temperature of 20°C.

By adding 727.5 g of a water and after heating for a few minutes, a clear solution is obtained.

EXAMPLE Xb

Crosslinking, using the crosslinking agent prepared in Example Xa, of the polyamino-amide polymer obtained by condensing adipic acid with diethylenetriamine.

472 g of an aqueous solution containing 83.8 g of the crosslinking agent prepared in Example Xa are added to 2,000 g of an aqueous solution containing 400 g (2.34 equivalents of amine) of the polyamino-amide prepared according to Example A.

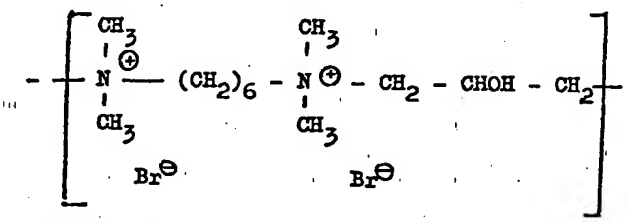
The reaction medium is stirred at 90°C and, after heating for 4 hours, gelling of the solution is observed.

The concentration of active material in the solution is rapidly brought back to 10% by adding 2,326 g of water.

A clear solution is obtained, which has a viscosity, at a rate of shear of 88.4 seconds^{-1}, of 0.64 Poise.

EXAMPLE 1a

The following rinse composition is prepared:

Compound of Example VIb	0.5 g of active material
	0.5 g of active material
$R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$	0.7 g
R: C_8 to C_{10} alkyl; n=mean statistical value of 3.5	
Acid phosphate ester of oxyethyleneated oleyl alcohol sold under the trade-mark "Divalin SO" by Messrs. Zschimmer and Schwarz	0.4 g
Water, q.s.p.	100 cc

The pH of this solution is 7—8.

This rinse composition is applied to hair which has been washed beforehand. Hair treated in this way can be combed out very easily. When dry, the hair is particularly bulky, glossy and easy to style.

EXAMPLE 1b

The following rinse composition is prepared:

Polymer obtained by condensing adipic acid with diethylenetriamine in equimolar amounts and crosslinking with 0.11 mol of epichlorohydrin peramine group (according to Example 1 of the main application)	0.5 g of active material
Compound of Example VIIIb	0.5 g of active material
$R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$	0.7 g
R: C_8 to C_{10} alkyl; n=mean statistical value of 3.5	
Acid phosphoric ester of oxyethyleneated oleyl alcohol, sold under the trade-mark "Divalin SO" by Messrs. Zschimmer and Schwarz	0.4 g
Water, q.s.p.	100 cc

The pH of this solution is 7—8.

This rinse composition is applied to hair which has been washed beforehand.

Hair treated in this way can be combed out very easily. When dry, the hair is particularly bulky, glossy and easy to style.

EXAMPLE 1c

An emulsion having the following composition is prepared:

"Vaseline" (Registered Trade Mark for liquid petroleum)	15 g
Partially sulphated cetyl/stearyl alcohol, sold under the trademark "Lanette wax"	2.5 g
Polyoxyethyleneated cetyl/stearyl alcohol containing 10 mols of ethylene oxide, sold under the trademark "Simulsol 1951 RD"	2.5 g
Compound of Example VIIb	0.7 g
Water, q.s.p.	100 g

The pH of this solution is 9.5.

The application to the hair of this "rinse" in the form of an emulsion, followed by rinsing, makes it possible to comb the hair out more easily, imparts softness to the hair and renders the hairstyle very full of life.

EXAMPLE 1d

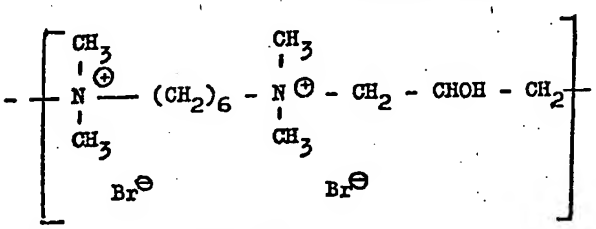
An emulsion having the following composition is prepared:

Vaseline oil	15 g
"Lanette wax" (partially sulphated cetyl/stearyl alcohol)	2.5 g
Polyoxyethyleneated cetyl/stearyl alcohol containing 10 mols of ethylene oxide, sold under the trademark "Simulsol 1951 RD"	2.5 g
Compound of Example IIIb	0.5 g
Water, q.s.p.	100 g

The pH of this solution is 9.

This "rinse" is applied to the hair, allowed to remain for a few minutes and then rinsed out. The hair can be combed out more easily and has a harder feel, and the hairstyle is more full of life.

EXAMPLE 2a



0.5 g of active material

Compound of Example VIb — 0.5 g of active material

Quaternary polyvinylpyrrolidone copolymer having a molecular weight of about 100,000 and marketed under the trademark "Gafquat 734" by Messrs. General Aniline — 0.4 g of active material

Perfume	0.2 g
Colorants	0.05 g
Water, q.s.p.	100 cc

The pH is 7.3.

When applied to hair which has been coloured, this wavesetting lotion makes the wet hair easier to comb out.

The dry hair is soft and easy to style. This softness effect remains after several shampoo treatments.

EXAMPLE 2b

The following wavesetting composition is prepared:

Compound of Example Ib	0.5 g of active material
Quaternary polyvinylpyrrolidone copolymer having a molecular weight of about 100,000 and marketed under the trademark "Gafquat 734" by Messrs. General Aniline	0.4 g of active material
Perfume	0.1 g
Colorants	0.01 g
Water, q.s.p.	100 cc

The pH is 7.3.

When applied to hair which has been coloured, this wavesetting lotion makes the wet hair easier to comb out. When dry, the hair is soft and easy to style. This softness effect remains after several shampoo treatments.

EXAMPLE 2c

The following wavesetting lotion composition is prepared:

Compound of Example IIb	0.6 g of active material
Quaternary polyvinylpyrrolidone copolymer having a molecular weight of about 100,000 and marketed under the trademark "Gafquat 734" by Messrs. General Aniline	0.5 g
Quaternised cellulose sold under the trademark "JR 400" by Messrs. Union Carbide	0.3 g
Ethyl alcohol, q.s.p.	15°
Perfume	0.1 g
Water, q.s.p.	100 cc

The pH is adjusted to 8.

When applied to hair which has been washed, this wavesetting lotion makes the hair easier to comb out. After drying and wavesetting, the hair is soft, glossy and easy to style. This effect remains after several shampoo treatments.

EXAMPLE 2d

The following wavesetting lotion composition is prepared:

Compound of Example IVb	0.3 g of active material
Quaternary polyvinylpyrrolidone copolymer having a molecular weight of about 100,000, marketed under the trademark "Gafquat 734" by Messrs. General Aniline	0.5 g
Quaternised cellulose sold under the trademark "JR 400" by Messrs. Union Carbide	0.3 g
Ethyl alcohol, q.s.p.	15°
Perfume	0.1 g
Water, q.s.p.	100 cc

The pH is adjusted to 8.

When applied to hair which has been washed, this wavesetting lotion makes the hair easier to comb out. After drying and wavesetting, the hair is soft, glossy and easy to style. This effect remains after several shampoo treatments.

EXAMPLE 3a

The following brushing lotion is prepared:

Compound of Example Vb	0.6 g of active material
Ethanol, q.s.p.	10°
Colorants	0.1 g
Perfume	0.1 g
Water, q.s.p.	100 g

The pH of the solution is adjusted to 7.

EXAMPLE 3b

The following brushing lotion is prepared:

Compound of Example IIIb	0.4 g of active material
Ethanol, q.s.p.	10°
Colorants	0.1 g
Perfume	0.1 g
Water, q.s.p.	100 cc

The pH of the solution is adjusted to 8.

EXAMPLE 3c

The following brushing lotion is prepared:

Compound of Example VIIIb	0.5 g of active material
Ethanol, q.s.p.	20°
Colorants	0.2 g
Perfume	0.1 g
Water, q.s.p.	100 cc

the pH of the solution is adjusted to 6.

EXAMPLE 3d

The following brushing lotion is prepared:

Compound of Example Ib	0.5 g of active material
Colorants	0.1 g
Perfume	0.1 g
Water, q.s.p.	100 cc

The pH of the solution is adjusted to 5.

EXAMPLE 3e

The following brushing lotion is prepared:

Compound of Example IIb	0.8 g of active material
Ethanol, q.s.p.	40°
Colorants	0.05 g
Perfume	0.1 g
Water, q.s.p.	100 cc

The pH of the solution is adjusted to 7.

EXAMPLE 3f

The following brushing lotion is prepared:

Compound of Example VIIb	0.6 g of active material
Colorants	0.05 g
Perfume	0.15 g
Water, q.s.p.	100 cc

The pH of the solution is adjusted to 6.

The brushing lotions to which Examples 3a—3f relate are applied to wet hair which has been dried without heat after shampooing. The head of hair is shaped, using a brush, whilst drying the hair using a hand-held drier.

It is found that the brush passes very easily through the hair and that the hairstyle holds for a long time. It is also found that the hair is glossy and soft.

EXAMPLE 4a

A shampoo having the following composition is prepared:

Triethanolamine C_{12}—C_{14} alkyl-sulphate	5 g
$R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$	5 g

R=C_9 to C_{12} alkyl; n=mean statistical value of 3.5

Lauryl diethanolamide	3 g
Compound of Example VIb	1 g
Perfume	0.1 g
Colorants	0.01 g
Water, q.s.p.	100 g

The pH is adjusted to 8 with triethanolamine.

This shampoo is in the form of a clear liquid. It makes the wet hair easier to comb out and imparts manageability and body to the hair.

EXAMPLE 4b

A shampoo having the following composition is prepared:

$R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$	10 g

R=C_9 to C_{12} alkyl; n=mean statistical value of 3.5

Copra diethanolamide	3 g
Colorant of Example IIIb	1 g of active material
Water, q.s.p.	100 g

The initial pH of 8.7 is brought back to a pH of 6 with lactic acid.

The shampoo is in the form of a clear liquid and is applied to natural hair. It makes the wet hair easier to comb out. The dried hair is bulky and full of life.

EXAMPLE 4c

A shampoo having the following composition is prepared:

Ammonium lauryl-sulphate	25 g
Diethanolamide of copra fatty acids	2 g
Compound of Example VIIIb	1 g of active material
Water, q.s.p.	100 g

The initial pH of 8.1 is brought back to a pH of 7.7 with lactic acid.

When applied to permed dyed hair, this slightly opalescent clear shampoo

ensures that the wet hair can be satisfactorily combed out. After drying, the hair is bulky and full of life.

EXAMPLE 4d

A shampoo having the following composition is prepared:

Polyoxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	5 g
Alkyl(C_{12}—C_{18})dimethylcarboxymethylammonium hydroxide, sold by Messrs. Henkel under the trademark "Dehyton AB 30"	10 g
Lauryl diethanolamide	3 g
Compound of Example Ib	0.8 g of active material
Water, q.s.p.	100 g

the initial pH of 7.8 is brought back to a pH of 6 with lactic acid.

This shampoo is in a slightly opalescent clear form and is applied to dyed hair. The wet hair is easy to comb out and softer. The dried hair is full of life, bulky and manageable.

EXAMPLE 4e

A shampoo having the following composition is prepared:

Triethanolamine alkyl(C_{12}—C_{14})-sulphate	12.5 g
Lauryl diethanolamide	2 g
Compound of Example IIb	0.7 g of active material
Water, q.s.p.	100 g

The spontaneous pH is 7.4.

When applied to natural hair, this clear liquid shampoo ensures that the wet hair can be combed out easily. It makes the wet hair slightly easier to comb out (sic). The dried hair is bulky, full of life and manageable.

EXAMPLE 4f

A shampoo having the following composition is prepared:

Alcohol (C_{12}—C_{14}) which is oxyethyleneated with 10 mols of ethylene oxide and is carboxymethylated, sold under the trademark Akypo RLM 100 by Messrs. Chem Y	3.5 g
Polyoxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	10 g
Compound of Example IIb	0.6 g of active material
Dimethyldiallylammonium chloride homopolymer having a molecular weight of about 100,000, sold under the trademark "Merquat 100" by Messrs. Merck	0.4 g of active material
Water, q.s.p.	100 g

The spontaneous pH is 7.4.

When applied to dyed hair, this liquid shampoo makes the wet hair easier to comb out. The dried hair is manageable and glossy.

EXAMPLE 4g

A shampoo is prepared, which has the same composition as in Example 4f except that 0.6 g of the compound of Example IIb is replaced by 0.5 g of the compound of Example VIIIb.

The properties of this shampoo are similar to those of the shampoo of Example 4f.

EXAMPLE 4h

A shampoo having the following composition is prepared:

Alcohol (C_{12}—C_{14}) which is oxyethylenated with 10 mols of ethylene oxide and is carboxymethylated, sold under the trademark "Akypo RLM 100" by Messrs. Chem Y	3.5 g
Polyoxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	10 g
Compound of Example 1b	0.6 g of active material
Dimethyldiallylammonium chloride homopolymer having a molecular weight of the order of 100,000, sold under the trademark "Merquat 100" by Messrs. Merck	0.4 g of active material
Perfume	0.15 g
Colorants	0.02 g
Water, q.s.p.	100 g

The pH is adjusted to 7.

When applied to dyed hair, this shampoo ensures that the wet hair is easy to comb out and renders the dry hair full of life and bulky.

EXAMPLE 4i

A shampoo having the following composition is prepared:

Hydroxypropylmethylcellulose	0.2 g
Diethanolamide of copra fatty acids	3 g
Triethanolamine alkyl(C_{12}—C_{14})-sulphate	10 g
Compound of Example VIIb	0.8 g of active material
Perfume	0.15 g
Colorants	0.01 g
Water, q.s.p.	100 g

The pH is adjusted to 7.8.

When applied to natural permed hair, this shampoo ensures that the wet hair is easy to comb out and renders the dry hair full of life and bulky.

EXAMPLE 4j

A shampoo having the following composition is prepared:

Polyoxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	7 g
$R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$ R=C_9 to C_{12} alkyl; n=mean statistical value of 3.5	7 g
Diethanolamide of copra fatty acids	2 g
Compound of Example IVb	0.8 g of active material
Perfume	0.1 g
Colorants	0.01 g
Water, q.s.p.	100 g

The pH is adjusted to 7.2.

When applied to dyed hair, this shampoo ensures that the wet hair is easy to comb out and renders the dry hair full of life and bulky.

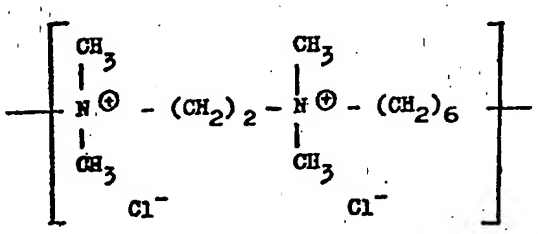
EXAMPLE 4k

A shampoo having the following composition is prepared:

$R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$	10 g

R=C_9 to C_{12} alkyl; n=mean statistical value of 3.5

Diethanolamide of copra fatty acids	3 g
Compound of Example IIb	0.5 g of active material



	0.2 g of active material
Water, q.s.p.	100 g

The spontaneous pH of 8.6 is brought back to a pH of 6 with lactic acid.

This shampoo is in the form of a clear liquid and is applied to natural hair. The wet hair is easy to comb out. When dry, the hair is well-cared for, manageable and glossy.

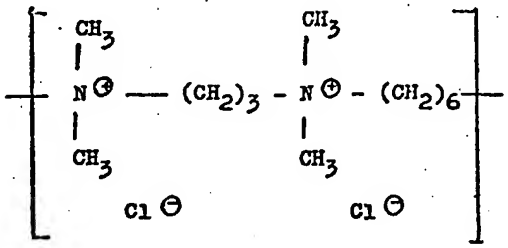
EXAMPLE 4l

A shampoo having the following composition is prepared:

$R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$	10 g

R= C_9 to 12 alkyl; n=mean statistical value of 3.5

Triethanolamine alkyl(C_{12}—C_{14})-sulphate	2 g
Diethanolamide of copra fatty acids	3 g
Compound of Example Ib	0.5 g of active material



	0.1 g of active material
Water, q.s.p.	100 g

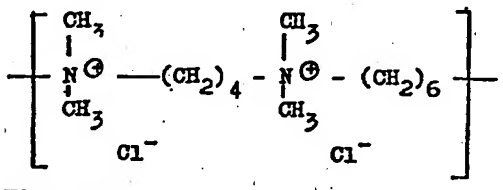
The initial pH of 7.9 is brought back to a pH of 6 with lactic acid.

This shampoo it in the form of a slightly opalescent liquid and is applied to dyed hair. The wet hair is easy to comb out and soft. The dried hair is full of life and bulky.

EXAMPLE 4m

A shampoo having the following composition is prepared:

Alcohol (C_{12}—C_{14}) which is oxyethyleneated with 10 mols of ethylene oxide and is carboxymethylated, sold under the trademark "Akypo RLM 100" by Messrs. Chem Y	3 g
Polyoxyethyleneated lauryl alcohol containing 12 mols of ethylene oxide	7 g
Lauryl diethanolamide	3 g
Compound of Example IIIb	0.6 g of active material



	0.3 g of active material
Water, q.s.p.	100 g

The initial pH of 4.5 is brought back to a pH of 7.2 with triethanolamine.

This shampoo is in the form of a clear liquid and is applied to dyed hair. the wet hair is easy to comb out. When dry, the hair is well-cared for and glossy.

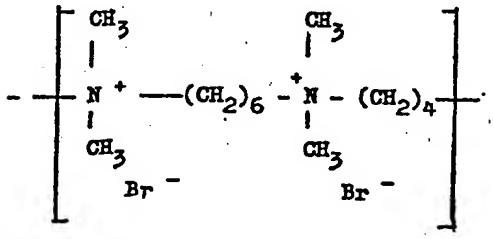
EXAMPLE 4n

A shampoo having the following composition is prepared:

$R—CHOH—CH_2—O—(CH_2—CHOH—CH_2—O—)_n—H$	10 g

R=C_9 to C_{12} alkyl; n=mean statistical value of 3.5.

Diethanolamide of copra fatty acids	2 g
Compound of Example Ib	0.7 g of active material



	0.3 g
Water, q.s.p.	100 g

The spontaneous pH is 7.

This shampoo is in the form of a clear liquid and is applied to natural permed hair. The wet hair is easy to comb out and soft. When dry, the hair is full of life, bulky and easy to manage.

EXAMPLE 4o

A shampoo having the following composition is prepared:

Triethanolamine C_{12}—C_{14}-alkyl-sulphate	10 g
Lauryl diethanolamide	2 g
Hydroxypropylmethylcellulose	0.2 g
Compound of Example Vb	0.8 g
Perfume	0.1 g
Colorants	0.01 g
Water, q.s.p.	100 g

The pH is adjusted to 8 with triethanolamine.

This clear liquid shampoo makes the wet hair easier to comb out. It ensures good manageability and dried hair which is well-cared for.

EXAMPLE 4p

A shampoo having the following composition is prepared:

Triethanolamine alkyl(C_{12}—C_{14})-sulphate	15 g
Hydroxypropylmethylcellulose	0.2 g
Lauryl diethanolamide	3 g
Compound of Example IXb	1 g
Perfume	0.2 g
Colorants	0.01 g
Water, q.s.p.	100 g

The spontaneous pH is 7.7.

EXAMPLE 4q

A shampoo having the following composition is prepared:

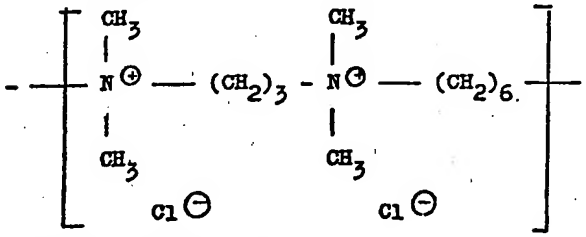
Triethanolamine alkyl(C_{12}—C_{14})-sulphate	10 g
Hydroxypropylmethylcellulose	0.3 g
Compound of Example Xb	1 g
Perfume	0.1 g
Colorants	0.015 g
Water, q.s.p.	100 g

The spontaneous pH is 7.7.

EXAMPLE 5a

Deep care cream after shampooing.

Cetyl alcohol	20 g
Oxyethyleneated cetyl alcohol containing 10 mols of ethylene oxide, sold under the trademark "Brij 50" (Atlas)	12 g



	1.5 g of active material
Compound of Example VIIb	0.5 g of active material
Acid phosphoric ester of oxyethyleneated oleyl alcohol, sold under the trademark "Divalin SO" by Messrs. Zschimmer and Schwarz	1 g
Water, q.s.p.	100 g

EXAMPLE 5b

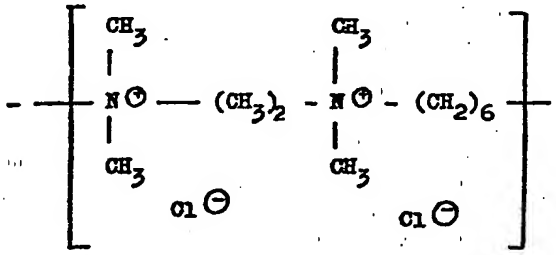
Deep care cream after shampooing.

Cetyl alcohol	22 g
Oxyethyleneated cetyl alcohol containing 10 mols of ethylene oxide, sold under the trademark "Brij 56" by Messrs. Atlas	10 g
Compound of Example IVb	0.5 g of active material
Acid phosphoric ester of oxyethyleneated oleyl alcohol, sold under the trademark "Divalin SO" by Messrs. Zschimmer and Schwarz	1.2 g
Water, q.s.p.	100 g

The care cream of Example 5a of Example 5b is applied to clean, damp hair, which has been dried without heat, in an amount (60 to 80 g) which is sufficient to thoroughly impregnate and cover the head of hair. It is allowed to remain for 30 to 40 minutes and rinsed out. The wet hair is very soft and easy to comb out. It is set in waves and dried under a drier. The dried hair can be combed out easily and has a silky feel; it is glossy, full of life and has body and bulk.

EXAMPLE 5c

Deep care cream before shampooing

Stearic acid	12 g
oxyethyleneated cetyl/stearyl alcohol containing 10 mols of ethylene oxide	4 g
Monoethanolamine	2 g
Glycerol	4 g
	1.2 g of active material
Compound of Example VIIIb	0.5 g of active material
Perfumes and colorants	
Water, q.s.p.	100 g

The pH is adjusted to 7.

EXAMPLE 5d

Deep care cream before shampooing.

Stearic acid	12 g
Oxyethyleneated cetyl/stearyl alcohol containing 10 mols of ethylene oxide	6 g
Monoethanolamine	3 g
Glycerol	3 g
Compound of Example IIIb	0.8 g of active material
Perfumes and colorants	
Water, q.s.p.	100 g

The pH is adjusted to 7.

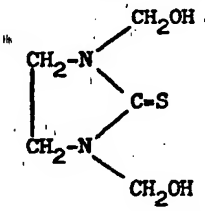
The care cream of Example 5c or 5d is applied at the rate of 60 grams to dirty, damp hair. The head of hair is thoroughly impregnated by massaging. The cream is allowed to remain for 30 minutes. Shampooing is carried out. The wet hair is very soft and easy to comb out. After wavesetting and drying, the hair has a particularly soft feel. It is glossy, full of life and has body. This effect remains after several shampoo treatments.

EXAMPLE 6a

Structuring lotion applied without rinsing

The following composition is prepared:

Dimethylolethylenethiourea of the formula:



	0.5 g
Quaternary polyvinylpyrrolidone copolymer having a molecular weight of about 1,000,000, marketed under the trademark "Gafquat 755" by Messrs. General Aniline	0.5 g
Compound of Example Ib	0.4 g of active material
Polyvinylpyrrolidone/vinyl acetate copolymer (70:30)	0.8 g
Phosphoric acid, q.s.p. pH 3	
Water, q.s.p.	100 cc

This lotion is applied to hair which has been washed and dried without heat after shampooing and before wavesetting. It is found that, in the wet state, the hair can be combed out easily and that it has a silky feel. After wavesetting and drying, the hair is glossy and full of life.

EXAMPLE 6b

This example is similar to Example 6a, with the difference that the compound of Example Ib is replaced by an equal amount of the compound of Example IVb.

EXAMPLE 7a

Non-rinsed lotion suitable for use before permanent waving.

Trimethylcetylammonium bromide	0.1 g
Compound of Example IVb	1.5 g
Perfume	0.1 g
Colorants	0.1 g
Citric acid, q.s.p. pH 5	
Water, q.s.p.	100 g

When applied to hair which has been washed, this non-rinsed product makes the hair easier to comb out and makes it possible for permanent waving to be carried out easily. It protects the hair, and the curl is held for a long time.

EXAMPLE 7b

Non-rinsed lotion suitable for use before permanent waving.

Trimethylcetylammonium bromide	0.15 g
Compound of Example VIIb	2.2 g
Perfume	0.2 g
Colorants	0.01 g
Citric acid, q.s.p. pH 4	
Water, q.s.p.	100 g

When applied to hair which has been washed, this non-rinsed product makes the hair easier to comb out and makes it possible for permanent waving to be carried out easily. It protects the hair, and the curl is held for a longer time.

EXAMPLE 8a

Permanent waving.

Reducing liquid:	
Thioglycolic acid	3 g
Thiolactic acid	2 g
22° Bé strength ammonia solution	4 g
Triethanolamine	3.5 g
Compound of Example VIb	1.4 g
Perfume	0.2 g
Colorants	0.05 g
Water, q.s.p.	100 g
Fixing liquid:	
Potassium bromate	9.5 g
Cetylpyridinium chloride	1 g
Tartaric acid, q.s.p. pH 6.5.	
Perfume	0.1 g
Colorants	0.05 g
Water, q.s.p.	100 g

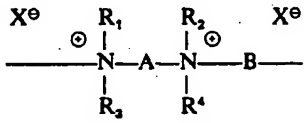
The reducing liquid is applied very easily to sensitised hair and penetrates deeply into the hair. After rinsing and application of the fixing liquid, a very strong and very uniform curl is observed. The hair is in a very attractive cosmetic condition. After drying, the hair is very soft and particularly glossy. The hairstyle is held particularly well.

EXAMPLE 8b

Reducing liquid:	
Thioglycolic acid	3.5 g
Thiolactic acid	2 g
22° Bé strength ammonia solution	3.5 g
Triethanolamine	4 g
Compound of Example VIIIb	2 g
Perfume	0.2 g
Colorants	0.01 g
Water, q.s.p.	100 g
Fixing liquid:	
Potassium bromate	8 g
Cetylpyridinium chloride	0.8 g
Tartaric acid, q.s.p.	pH 6.5
Perfume	0.2 g
Colorants	0.05 g
Water, q.s.p.	100 g

The reducing liquid is applied very easily to sensitised hair and penetrates deeply into the hair. After rinsing and application of the fixing liquid, a very strong and very uniform curl is observed. The hair is in a very attractive cosmetic condition. After drying, the hair is very soft and particularly glossy. the hairstyle is held partciularly well.

In our Application No. 8147/78 (Serial No. 1,604,471) we described and claim a process for conditioning the hair which comprises applying thereto a composition which comprises at least one crosslinked polyamine-amide and at least one cationic polymer having a molecular weight of at least 1500 comprising repeat units of the formula:

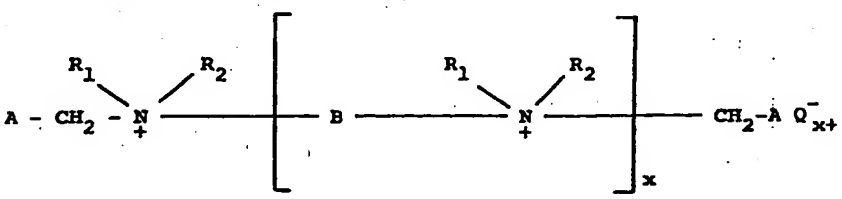


in which each of R_3 and R_4, which are identical or different, represents an alkyl radical having 1 to 3 carbon atoms, each of R_1 and R_2, which are identical or different, represents an alkyl radical having 1 to 3 carbon atoms, or a hydroxyalkyl radical having 1 to 3 carbon atoms, and, if $R_2=R_4=CH_3$ and $R_1=R_3$, R_1 and R_3 can also represent an alkyl group having 4 to 8 carbon atoms, and, if $R_2=R_4=R_1=CH_3$

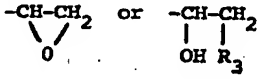
R_3 can also represent a benzyl group, a cyclohexyl group, or an alkyl group having 4 to 12 carbon atoms, and each of A and B, which are identical or different, represents a linear or branched alkylene radical having 2 to 20 carbon atoms in the chain, or a $-(CH_2)_n-Z-(CH_2)_n-$, $-CH_2-C_6H_4-CH-$ or $-CH_2-CH(OH)-CH_2-$ radical, n being 2 or 3, and Z representing either the —O— group or the —NH—CO—NH— group, and X represents an anion..

No claim is made herein to this process.

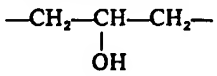
Also in our Application No. 8148/78 (Serial No. 1.604.472) we describe and claim a process for treating the hair which comprises applying thereto a composition which comprises at least one water-soluble polyamino-amide derivative which is the condensation product of a polyalkylene-polyamine with a polycarboxylic acid, said product having been reacted with a bifunctional alkylating agent of the formula:



in which x is 0 or an integer from 1 to 7, A denotes a



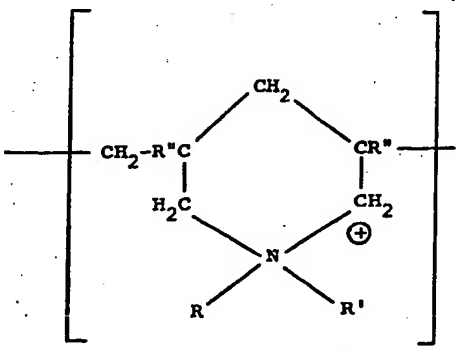
group in which R_3 denotes halogen, R_1 and R_2 denote, independently of one another, an alkyl or hydroxyalkyl group containing 1 to 4 carbon atoms, and B represents an alkylene group containing 2 to 6 carbon atoms, a



group, or a group of formula:

$$-(CH_2)_y-NH-CO-NH-(CH_2)_y-$$

in which y is an integer from 1 to 4 and Q denotes halogen, sulphate or methosulphate, and at least one water soluble high molecular weight (as hereinbefore defined) quaternary ammonium homopolymer of copolymer containing chain recurring units of the formula:



(I)

in which R'' denotes a hydrogen atom or a methyl group, and R and R' denote, independently of one another, an alkyl group having from 1 to 22 carbon atoms, a

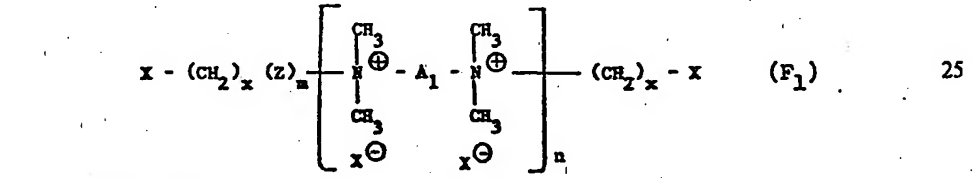
hydroxyalkyl group, or a lower amidoalkyl group, or R and R' together with the nitrogen atom to which they are bonded, denote a heterocyclic group, said units being associated with a cosmetically acceptable anion.

No claim is made herein to this process either.

Subject to these disclaimers:—

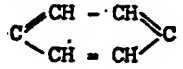
WHAT WE CLAIM IS:—

1. A process for conditioning human hair which comprises applying thereto a composition comprising, in a compatible vehicle, a polyamino-polyamide polymer prepared by crosslinking a polyamino-polyamide obtained by the polycondensation of one or more acid compounds, selected from:
(i) an organic dicarboxylic acid, (ii) an ethylenically unsaturated aliphatic mono- or di-carboxylic acid, (iii) an ester of an acid as defined under (i) or (ii), (iv) a mixture of two or more compounds defined under (i), (ii) or (iii) or (v) the product of reaction of a bisprimary amine or a bis-secondary diamine with (i), (ii), (iii) or (iv), with one or more polyamines selected from a bis-primary, mono- or di-secondary polyalkylene-polyamine up to 50 mol % of this polyamine optionally being replaced by a bis-primary amine or bis-secondary diamine with the proviso that the maximum percentage is 20 mol % when the amine is hexamethylene diamine, the crosslinking agent being:
(I) a simple bifunctional compound which is either (1) a bis-halogenohydrin resulting from the reaction of an epihalogenohydrin with a primary amine, a bis secondary diamine, a bis-phenol or a bis-mercaptan, (2) a bis-azetidinium compound, (3) a bis-halogenoacyldiamine, or (4) a compound represented by the general formula:



(F_1)

in which X denotes Cl or Br, Z denotes



x is 1 to 3, m is 0 or 1, and n is 0 or 1, such that m and n cannot simultaneously be 1 and when m is 1, x is 1; and A_1 denotes either a divalent saturated C_2, C_3, C_4 or C_6 hydrocarbon radical or a 2-hydroxypropylene radical;
(II) an oligomer obtained by reacting a compound (a), which is a compound as defined under (1), (2), (3) or (4) above, or (5) an epihalogenohydrin, (6) a bis-epoxide or (7) a bis-unsaturated compound, with a compound (b) which is a primary amine, a bis-secondary diamine, a bis-mercaptan or a bis-phenol, the molar ratio of (b):(a) being from 0.1:1 to 0.9:1;
(II bis) an oligomer obtained by reacting a compound (a_1), which is a compound as defined under (1), (3), (4) or (6) above, with a bis-tertiary diamine (b_1), the molar ratio of (b_1):(a_1) being from 0.1:1 to 0.9:1, and
(III) the product resulting from the quaternisation of a compound (a_2), which is either (1') a bis-halogenohydrin resulting from the reaction of an epihalogenohydrin with piperazine, a bis-phenol or a bis-mercaptan, (2) a bis-azetidinium compound, (3) a bis-halogenoacyldiamine, (4) a bis-(alkyl halide) of formula (F_1), (6) a bis-epoxide, (7) a bis-unsaturated compound, (8) an oligomer (II) obtained by reacting a compound (a_3), which is a compound as defined under (1), (2), (3), (4), (6) or (7) above, with a compound (b_3) which is a primary amine, a bis-secondary diamine, a bis-mercaptan or a bis-phenol, the molar ratio of (b_3):(a_3) being from 0.1:1 to 0.9:1, (9) an oligomer obtained by reacting an epihalogenohydrin (compound a_4) with a bifunctional compound (b_4) which is piperazine, a bis-mercaptan, a bis-phenol or a piperazine bis-epoxide, the molar ratio of compound (b_4):epihalogenohydrin being from 0.1:1 to 0.9:1, and (10) an oligomer obtained by reacting a compound (a_5), which is either (1') a bis-halogenohydrin resulting from the reaction of an epihalogenohydrin with

piperazine, a bis-phenol or a bis-mercaptan, (2) a bis-halogenoacyldiamine, (3) a bis-(alkyl halide) of formula (F_1), or (4) a bis-epoxide, with a bis-tertiary diamine (b_6), said compound (a_2) containing tertiary amine groups which can be alkylated with an alkylating agent (c) which methyl or ethyl chloride. bromide, iodide, sulphate, mesylate or tosylate, benzyl chloride or bromide, ethylene oxide, propylene oxide and glycidyl, the molar ratio (b_5):(a_5) being from 0.1:1 to 0.9:1, said polyamino-polyamide possessing the following characteristics:

(1) it is completely soluble in water to a concentration of 10% without gel formation;

(2) the viscosity of a 10% aqueous solution of the polymer at 25°C is at least 3 centipoises; and

(3) it does not possess any reactive group and, in particular, it does not have any alkylating groups and is chemically stable.

2. A process according to claim 1 in which the acid compound is chosen from adipic acid, terephthalic acid, or an ester therof, or the product resulting from the addition of ethylenediamine to acrylic, methacrylic or itaconic acids or an ester thereof.

3. A process according to claims 1 or 2, in which the polyalkylenepolyamine is diethylenetriamine, dipropylenetriamine or triethylene tetramine, or a mixture thereof with ethylenediamine, hexamethylenediamine or piperazine.

4. A process according to any one of claims 1 to 3, in which the polyamino-polyamide is obtained by condensing adipic acid with diethylenetriamine.

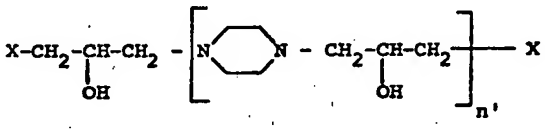
5. A process according to any one of claims 1 to 4, in which the polyamino-polyamide has been crosslinked to the extent of 0.025 to 0.35 mol of crosslinking agent per amine group of the polyamino-polyamide.

6. A process according to claim 5 in which the polymer has been crosslinked to the extent of 0.025 to 0.2 mol of crosslinking agent per amine group of the polyamino-polyamide.

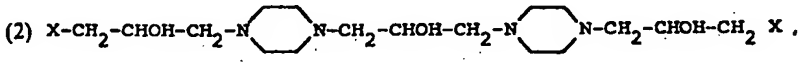
7. A process according to claim 5 in which the polymer has been crosslinked to the extent of 0.25 to 0.1 mol of crosslinking agent per amine group of the polyaminopolyamide.

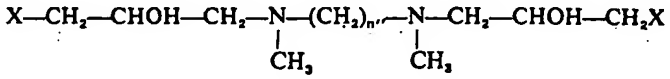
8. A process according to any one of claims 1 to 7 in which the crosslinking agent is:

a bis-halogenohydrin of the formulae:

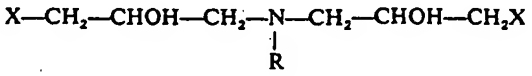
(1) 

in which N' is 1 to 4,

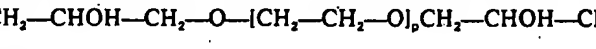
(2) 

(3) 

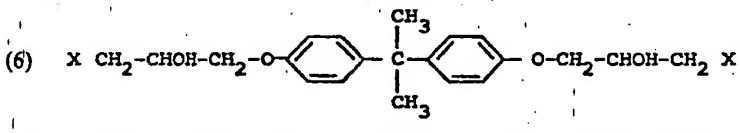
in which n'' is 2 to 6,

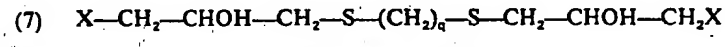
(4) 

in which $R=C_nH_{2n+1}$ and n=1 to 18, or $R=-(CH_2-CH_2-O)_mH$ and m=1 or 2,

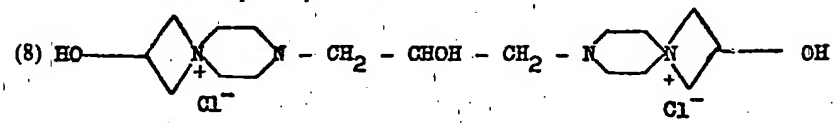
(5) 

in which p is 0 to 25,

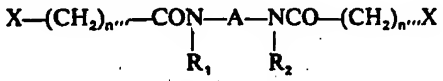
(6) 

(7) 

in which q is 2 to 6, and X denotes Cl or Br;
a bis-azetidinium compound of the formula:

(8) 

a bis-halogenoacyldiamine of the formula:

(9) 

in which X=Cl or Br, A=—CH_2—CH_2—, —CH_2—CH_2—CH_2— or

n'''=1 to 10, and R_1=R_2=H, or R_1 and R_2 together denote the ethylene radical; with the proviso that when A denotes —CH_2—CH_2—CH_2— or

R_1 and R_2 must denote hydrogen or a compound of formula (F_1).

9. A process according to any one of claims 1 to 8 in which compound (b) is a primary amine, a bis-secondary diamine or a bis-mercaptan.

10. A process according to any one of claims 1 to 8 in which compound (b) is piperazine or ethane-1,2-dithiol.

11. A process according to any one of claims 1 to 8 in which compound (a) is a compound (1), (2) bis-azetidinium, (3), (4), (5), or (6) and compound (b) is a bis-phenol.

12. A process according to claim 11 in which compound (b) is bis-phenol A or 2,2-(4,4'-dihydroxydiphenyl)-propane.

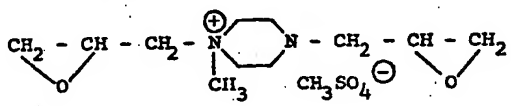
13. A process according to any one of claims 1 to 7 in which compound (b_1) is a bis-tertiary diamine.

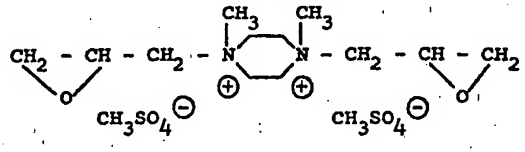
14. A process according to claim 13 in which the compound (b_1) is N,N,N',N'-tetramethyl-ethylene-, -propylene-, -butylene- or -hexamethylene-diamine.

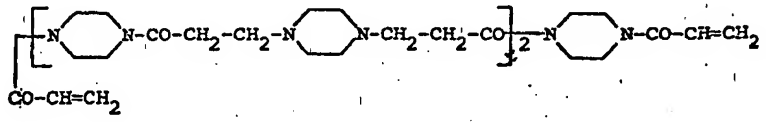
15. A process according to any one of claims 1 to 14 in which the alkylating agent (c) is dimethyl sulphate.

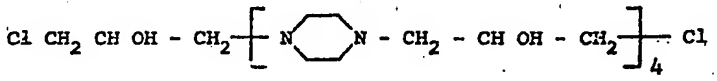
16. A process according to any one of claims 1 to 11 in which the modified bis-azetidinium compound is derived from a bis-halogenohydrin in which the halogenohydrin units are bonded to the remainder of the molecule by tertiary nitrogen groups, and contains either two azetidinium groups or one azetidinium group and one halogenohydrin group.

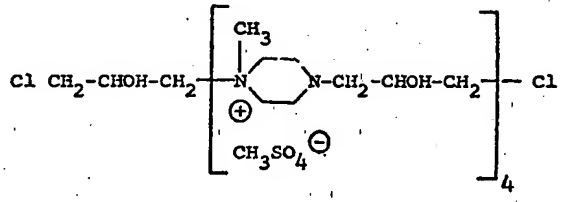
17. A process according to any one of claims 1 to 7 in which the crosslinking agent is a compound of the formula:

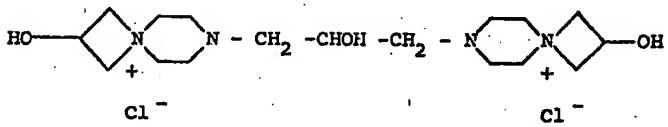
(1) 

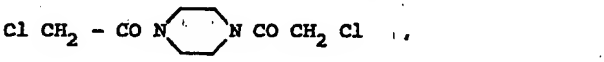
(2) 

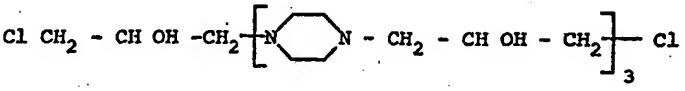
(3) 

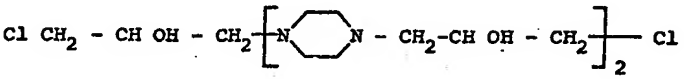
(4) 

(5) 

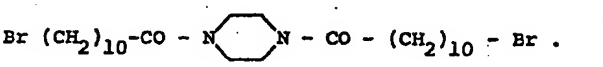
(6) 

(7) 

(8) 

(9) 

or

(10) 

18. A process according to any one of claims 1 to 17 in which the polymer is one specifically identified herein.

19. A process according to any one of claims 1 to 18 in which the composition is in the form of a shampoo and contains a non-ionic, anionic, cationic, amphoteric or Zwitter-ionic surface-active agent.

20. A process according to any one of claims 1 to 18 in which the composition contains a hair restructuring agent.

21. A process according to any one of claims 1 to 20 in which the composition has a pH of 2 to 11.

22. A process according to claim 21 in which the composition has a pH of 3 to 8.

23. A process according to any one of claims 1 to 22 in which the composition contains 0.1 to 5% by weight of the crosslinked polymer based on the total weight of the composition.

24. a process according to any one of claims 1 to 23 in which the composition contains a water-soluble electrolyte.

25. A process according to claim 24 in which the electrolyte is a sodium, potassium, ammonium or calcium chloride or acetate.

26. A process according to claim 24 or 25 in which the electrolyte is present in an amount from 0.01 to 5% by weight based on the total weight of the composition.

27. a process according to any one of claims 1 to 26 in which the composition contains a cosmetic polymer.

28. A process according to any one of claims 1 to 27 in which the composition contains at least one of a perfume, colorant, sequestering agent, thickener, anionic, cationic, amphoteric, Zwitter-ionic or non-ionic surface-active agent, synergistic agent, foam stabiliser or softening agent.

29. a process according to any one of claims 1 to 28 in which the composition is in the form of an aqueous or aqueous-alcoholic solution, a cream, a gel, a dispersion, an emulsion or an aerosol.

30. A process according to claim 1 substantially as described in any one of Examples 1a to 8b.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn,
London WC1R 5EU.

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